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Relaxation of mechanical stress by fracture as a reason for autolocalization of topochemical solid state reactions [1]

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Abstract

The present investigation of the dehydration of the model subject, namely, glass-like sodium hydrate silicate, has shown that the relaxation of mechanical stresses by fracture is a reason of localization and autolocalization of the topochemical process.

The elucidation of the causes of localization and autolocalization determining the specificity of development of topochemical processes through the formation and growth of nuclei is one of the urgent problems of modern solid state chemistry [1, 2]. Solving this problem requires an understanding of the mechanism of nucleation and the nature of nuclei, or reaction centres, as they are also termed, during solid state chemical reactions.

The up-to-date background of nucleation and nuclei growth, in particular, for dehydration which is to be considered, and also for other processes, is based on the classical theory of nucleation during phase transitions of the first type. At the same time, the incorrectness of applying this theory to solid state chemical reactions has been repeatedly noted [3].

In our opinion, in order to understand the causes and nature of nucleation, we should study such a model system in which a reaction would proceed involving all the features of the dehydration of crystallohydrates which have become models in topochemistry [3] ($CuSO_4 \cdot 5H_2O$; $Li_2SO \cdot H_2O$; alums) but without complicating factors such as the transformation of the parent crystalline structure to the product. We have chosen the dehydration of glass-like sodium silicate hydrate as such a model system to adequately represent the dehydration of real hydrates. To prepare glass-like sodium silicate hydrate samples, an aqueous solution of sodium silicate was poured into special forms and left to stand for 3 months until constant mass in a desiccator over $CuSO_4 \cdot 3H_2O$ was obtained. In this way,

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[1] Dedicated to Hans Georg Wiedemann.

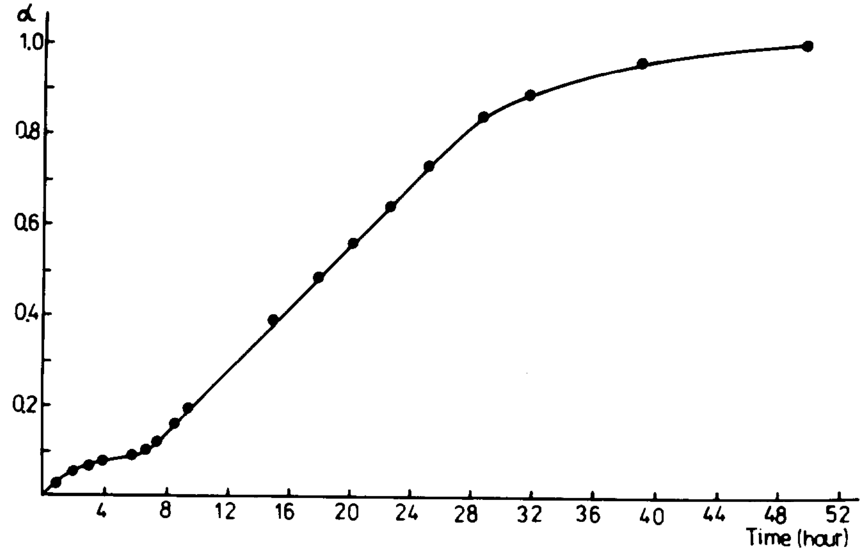


Fig. 1. Degree of conversion, $\alpha = m_{H_2O}(t)/m_0$, versus time for glass-like sodium silicate hydrate decomposed isothermally at 25°C in vacuo.

transparent discs 15 mm in diameter and 4 mm thick were obtained. The dehydration process was conducted at a temperature of +25°C in vacuo.

It has been established that the time dependence of α behaves as a sigmoidal curve as is usual for topochemical processes, and has a pronounced induction period (Fig. 1) during which the loss of water occurs at a slow rate. For this stage of the process the experimental time dependence of $m_{H_2O}(t)$ plotted on the $m_{H_2O}(t)-\sqrt{t}$ coordinates is shown in Fig. 2 and is described by the kinetic equation of removal of a diffusing component from the medium in an approximation of half-space for linear boundary conditions of the third type [4], which can be written in the general form as

$$\frac{m(t)}{m_0} = \frac{D}{kl}\left[\exp\left(\frac{k^2}{D}t\right)\operatorname{erfc}\left(\frac{k}{\sqrt{D}}\sqrt{t}\right) + \frac{2k}{\sqrt{\pi}\sqrt{D}}\sqrt{t} - 1\right] \tag{1}$$

Expression (1) can be brought into a more convenient form. At

$$\frac{k}{\sqrt{D}}\sqrt{t} \ll 1$$

$$\alpha(t) = \frac{m(t)}{m_0} = \frac{kt}{l}$$

and at $\frac{k}{\sqrt{D}}\sqrt{t} > 2.8$

$$\alpha(t) = \frac{m(t)}{m_0} = \frac{2\sqrt{Dt}}{l\sqrt{\pi}} - \frac{D}{kl}$$

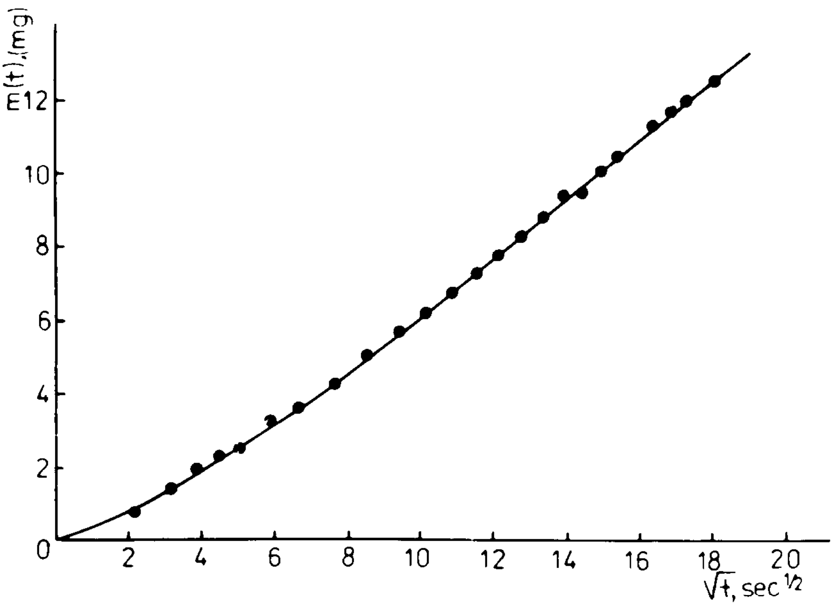


Fig. 2. Plot of $m_{H_2O}(t)$ (loss of water during the induction period) versus square root of time.

where k is the constant of transition of a molecule from the solid to the gaseous phase, D is the diffusion coefficient and l is the thickness of the sample.

Such a character of the kinetics of the process, i.e. the initial slow removal of water during the induction period described by the equation of removal of a diffusing component from the medium and sigmoidal form of the general kinetic curve, has also been observed in other works concerned with studying the dehydration of crystallohydrates [5, 6]. Thus, it may be argued that the dehydration of glass-like sodium silicate hydrate adequately describes the kinetics of dehydration of crystalline hydrates. A characteristic feature of the dehydration of glass-like sodium silicate hydrate is that the process of water removal and the transformation from the parent substance to the reaction product is not accompanied by structural changes which, as a rule, occur during the dehydration of crystallohydrates. The lack of a stage of transformation of the parent crystalline structure to the product provides a better insight into the processes occurring during dehydration.

A microscopic observation of samples of glass-like sodium silicate hydrate during dehydration has shown that after the time interval corresponding to the induction period, cracks occur at random sites on the surface, and all the subsequent cracks originate on the surface of the previous one, move perpendicular to it for a distance of 40 μm, turn left or right with equal probability and then prodeed along the direction of

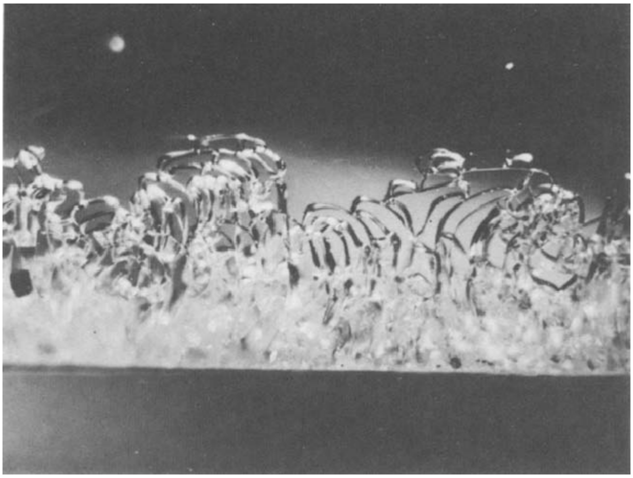


Fig. 3. Self-organization of cracks on the surface of glass-like sodium silicate hydrate during dehydration (magnification ×40).

propagation of the previous crack (Fig. 3). It may be argued that after the first crack occurs, further crack formation and propagation occurs in a self-organized way. In the final analysis, such a character of self-organization of the process leads to the formation of several individual aggregates of cracks on the surface of the samples (Fig. 4). As the dehydration proceeds further, these regions of crack aggregates grow and coalesce, finally covering the entire surface. As a result, a front of dehydration forms and moves deep into the samples.

Thus, it is seen that the dehydration of glass-like sodium silicate hydrate is a typical topochemical process. On the basis of experimental facts (the

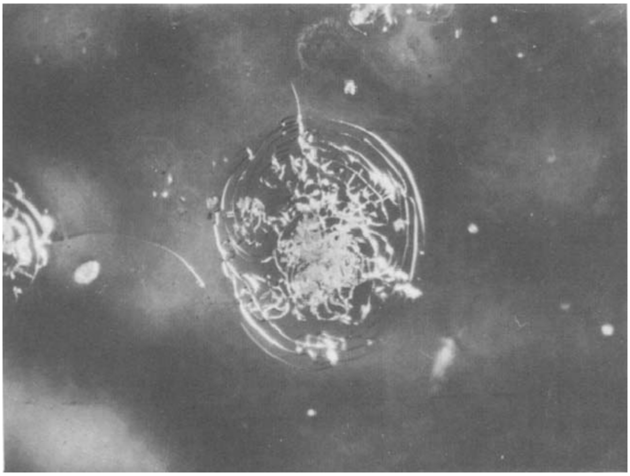


Fig. 4. Nucleus of dehydration as a result of the hydrate crossed by cracks (magnification ×60).

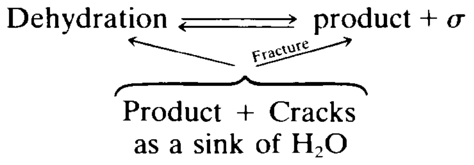
kinetics of water removal during the induction period and the spatial propagation of the process as a self-organized evolution of cracks) the following model of dehydration is proposed. During the induction period, a surface layer, depleted of water and having a diffusion profile of distribution of water molecules, forms on the hydrate surface. The removal of water is accompanied by a shrinkage and hence the layer depleted of water is in a stress-deformed state. As the thickness of the layer depleted of water grows, the diffusion difficulties for the removal of water are aggravated, and as a result the dehydration process is retarded.

The occurence of cracks in the stressed, water depleted surface layer eliminates the diffusion difficulties and the induction period ceases. The surface of cracks becomes a sink just as the parent hydrate surface is in the very initial instance of the reaction. The formation of a crack distrubs the homogeneous-stressed state of the hydrate surface in the region of the crack. The dehydration of the surface of a crack leads to a complex-stressed state, which results predominantly in the formation of subsequent cracks within the surface of the previous crack. A feedback occurs between the reaction and the formation of cracks, which leads to their self-organization.

Due to this feedback, autolocalization of the process occurs and a nucleus (reaction centre or dehydration figure) which is a region of the hydrate crossed by cracks is formed. As shown experimentally in the present work, the topochemical character of the process (formation and growth of nuclei) is due to the relaxation of mechanical stresses by the fracture of the surface hydrate layer stressed because of the progress of the chemical process.

This work is a logical extension of previous works [7, 8] which covered the influence of mechanical stresses σ occurring during solid state transformation on their kinetics. The proposed phenomenological scheme describing the influence of stresses on the kinetics of solid state transformation can easily be extended to the dehydration of crystallohydrates on the basis of the proposed model of dehydration shown in Scheme 1.

The diffusion removal of water from the crystallohydrate at the initial stage gives rise to the concentration stresses in the surface layer. The relaxation of these stresses by fracture eliminates the diffusion difficulties,



Scheme 1.

approaching the sink (of a crack) to the region with the initial concentration of water. The dehydration of the surface of the crack gives rise to the cracks of the following generation and so on (feedback between the reaction and cracks occurs).

Thus, the present investigation of the dehydration of the model compound, glass-like sodium silicate hydrate, has shown experimentally that the relaxation of mechanical stresses by fracture is a reason for localization and autolocalization of the topochemical process.

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